

A technique for obtaining the Raman spectra of liquids and solutions under high pressure

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Abstract—This note describes the design and use of a cell to obtain the Raman spectra of solutions and liquids under high pressure.

THERE IS NOW a considerable body of literature devoted to the thermodynamic and electrochemical properties of pure liquids and solutions under conditions of high pressure [1–3]. Nevertheless, few attempts have been made to use vibrational spectroscopy to obtain a more detailed understanding of the molecular processes involved. Infrared spectroscopy has been used to study the effects of pressure on solids [4] and liquids [5–7] and, although some attempts have been made to utilise Raman spectroscopy [8–12], the results have usually been qualitative in nature [13–15]. Perhaps the most serious technical difficulty in the use of i.r. spectroscopy at high pressures is the choice of window material.

Sapphire and quartz, which have high mechanical strength, are limited in their transparency in the i.r. region of the spectrum. Diamond is probably the only material that has a suitable combination of mechanical strength and good i.r. transmitting properties. In recording the i.r. spectra of liquids under pressure, it is also necessary to ensure that the pathlength of the cell does not change with pressure [16].

The use of Raman spectroscopy to obtain vibrational spectra under pressure has distinct advantages over i.r. spectroscopy. First, since exciting and Raman scattered radiation both occur in the visible region of the spectrum, sapphire or quartz windows

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may be used. Second, the difficulties posed by pathlength changes due to pressure are no longer a serious problem with Raman spectroscopy, relative to those associated with i.r. spectroscopy.

The following Raman technique was designed to make use of the above facts with a laser as an excitation source, and to incorporate more precise pressure and temperature measurement than previously employed.

EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. The basic cell is an American Instrument Company stainless steel, two-window, 3.0 kbar optical absorption cell (3.5 in. o.d. \times 1 in. i.d. \times 5 in. long). A two-window configuration, with the

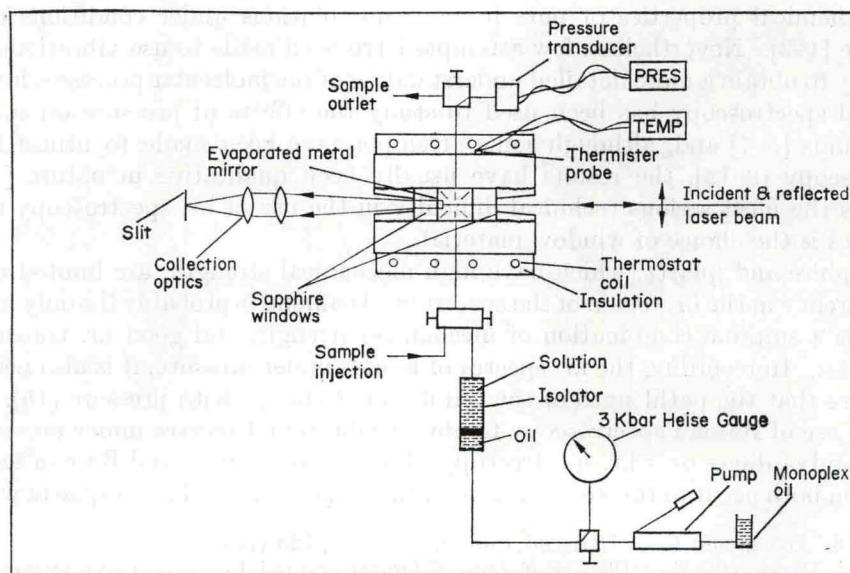


Fig. 1. Schematic diagram of high pressure Raman cell and ancillary measuring equipment.

windows on the same optical axis, is economical to construct and easier to use than one involving three or more windows. This window configuration results in the Raman scattered light being observed at 0° or 180° to the exciting radiation. The technique reported here involves collection of Raman scattered light at 180° to the initial exciting radiation direction. Initially, the laser beam was allowed to pass through the sample and into the spectrometer. This arrangement resulted in the presence of very intense plasma lines obscuring the Raman spectrum. This difficulty was overcome by the use of a small metal mirror evaporated onto the surface of the sapphire window closest to the collection optics. The mirror reflects the laser beam back out of the cell. This procedure not only prevents the direct entry of the exciting beam into the spectrometer, but also increases the Raman intensity, since the laser beam makes two passes through the sample.